

# ***Dry Reforming of Methane in a Microwave-Assisted Fluidized Bed Reactor: Experimental, Thermodynamic and Kinetic Analysis***

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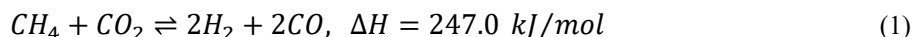
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## ***Highlights***

- Dry reforming methane (DRM) as an ecological method for syngas production.
- Potential of fluidized bed reactor and microwave heating in DRM.
- Bifunctional Fe/C catalyst for microwave-assisted DRM.

## **1. Introduction**

One of the most important challenges facing the chemical industry is the implementation of sustainable development principles, including the use of renewable electricity for the production of fuels and chemicals and the decarbonization of industrial processes. In this context, dry reforming of methane (DRM) is a particularly attractive route for synthesis gas (H<sub>2</sub>/CO) production, as it simultaneously utilizes two major greenhouse gases, CH<sub>4</sub> and CO<sub>2</sub> (Eq. 1).



Syngas is a key feedstock for the synthesis of methanol, ammonia, and Fischer-Tropsch fuels. However, two major challenges associated with DRM are its high endothermicity and catalyst coking, leading to low effectiveness, and catalyst deactivation, respectively.

This work is conducted within the framework of the EU funded TITAN project aimed at the direct conversion of biomethane into green hydrogen and carbon materials using a microwave-assisted fluidized bed reactor (FBR).

## **2. Methods**

DRM was carried out in a microwave-assisted FBR using an Fe/C catalyst synthesized at CNRS. Microwaves were transmitted through a single-mode microwave line based on a WR975 waveguide. The microwave line consisted of a 915 MHz solid-state microwave generator with a maximum power of 1300 W, a manual three-stub tuner and a sliding short circuit, and a custom designed monomode microwave applicator housing a quartz FBR containing the catalytic bed.

An alumina refractor cylinder was placed around the quartz reactor tube to reduce radiative heat losses at high operating temperatures. The temperature of the catalytic bed was measured by a pyrometer. The forward and reflected microwave powers were also monitored and the reflected power was continuously adjusted to its minimum value.

The FBR was fed with various mixtures of CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>. The reactor outlet gases were sampled and analyzed using a gas chromatograph (Inficon, USA), allowing the testing of H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub>.

Under microwaves, the Fe/C catalyst has a double function: the iron core acts as an efficient microwave susceptor, which absorbs electromagnetic energy and turns it into heat, while the tightly adhered carbon shell provides the catalytic activity.

The reaction kinetic experiments were conducted in a thermobalance - TG 209 F1 Libra (Netzsch, Germany) coupled with the GC.

The method of minimizing the Gibbs free energy was used to calculate the equilibrium gas compositions and carbon yields in DRM.

$$\min G_{T,P}^t = f(n_1, n_2, \dots, n_i, \dots, n_N, n_C) \quad (14)$$

where  $n_i$  is the number of moles of the  $i$ -th chemical species. The minimization involved  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{C}$ , since all side reactions associated with DRM include only these species.

### 3. Results and discussion

Figure 1 presents selected thermodynamic and kinetic results obtained from the performed investigations. Thermodynamic analysis identifies equilibrium limits on conversion, product distribution, and carbon formation however, it does not account for the presence of the catalyst. In addition, it shows that the performance of DRM strongly depends on operating parameters such as temperature, pressure, and gas feed composition. In contrast, kinetic studies provide rate equations that are essential for reactor modelling.



**Figure 1.** Thermodynamic (left) and reaction kinetic (right) results.

Experimental results highlight the effect of microwave power on the temperature of catalyst bed and  $\text{CH}_4$  and  $\text{CO}_2$  conversions

Preliminary experiments will use this framework to assess mainly the effect of microwave power and temperature on  $\text{CH}_4$  and  $\text{CO}_2$  conversions,  $\text{H}_2/\text{CO}$  ratios, and catalyst stability. By integrating the thermodynamic limits with kinetic insights, the study will enable tuning of operating conditions and prediction of carbon deposition trends, as such providing a robust methodology for future experimental work. In addition, we carried out a comparative study using the same reactor size and catalyst amount, but by heating with a conventional electrical furnace. Catalytic performances follow the same trends for MW and conventional heating methods. However, MW heating achieve higher conversion which can be attributed to the overcoming of heat transfer limitation.

### 4. Conclusions

From the outset of the TITAN project, operation at 915 MHz was selected because, in terms of energy efficiency and the maximum output power achievable with commercial magnetron-based generators, this frequency is the most suitable for a future industrial installation. In addition, MW heating is not only a fully electrified technology, but initial laboratory tests have shown that the MW energy is absorbed selectively by the catalyst, without significant losses, thus overcoming the limitations of heat transfer associated with conduction potentially offering a more efficient alternative to the bulk heating achieved by conventional method.

#### Keywords

dry reforming methane; Fe/C catalyst; microwave heating; fluidized bed; 915 MHz

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